were indeed specifically predicted by Ringwood in 1966 (10). The "precipitation" hypothesis is a close relative of the fission hypothesis, since it maintains that the material now in the moon was ultimately derived from the earth, not from the mantle but from the earth's massive primitive atmosphere.

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## **Crystallization of Some Lunar Mafic**

Magmas and Generation of Rhyolitic Liquid

Abstract. During crystallization of lunar crystalline rocks 10022 and 10024, augite changes in composition almost continuously from titanaugite ( $\sim Ca_{36}Mg_{47}$  $Fe_{17}$  with  $TiO_{g} \sim 3$  percent) to a very iron-rich variety ( $Ca_{g}Mg_{5}Fe_{86}$ ), pigeonite changes from  $Ca_{9}Mg_{66}Fe_{25}$  to  $Ca_{10}Mg_{51}Fe_{39}$ , and olivine changes (in 10022) from  $Mg_{71}Fe_{29}$  to  $Mg_{11}Fe_{59}$ , whereas plagioclase stays as bytownite. These compositional variations, as well as the textural relations, may be explained by rapid crystallization of undercooled magmas. The residual liquids found as mesostasis are rhyolitic, which suggests that fractional crystallization of some lunar mafic magmas can generate rhyolitic magmas. Melting experiments were made on crystalline rocks to determine liquidus temperatures and crystallizing phases.

Crystalline rocks 10017,20 and 10024, 23 [type B (1)] and 10022,41 and 10072,33 (type A) were examined with microscope and microprobe analyzer. This paper reports mainly the analytical results for 10022 and 10024. Major



minerals of 10022 are titanaugitesubcalcic ferroaugite, pigeonite, ilmenite, plagioclase, olivine, troilite, native iron, and apatite. Those of 10024 are the same as those of 10022 except that olivine is absent and there are relatively large cristobalite crystals. All the rocks have many interstices filled with mesostasis, that is, fine-grained aggregates of potassium-rich phase and plagioclase with or without ilmenite, iron-rich clinopyroxene, nearly pure SiO<sub>2</sub> phase, troilite, native iron, apatite, and a Zrand Ti-rich mineral (possibly ZrTiO<sub>4</sub>). The minerals of 10017 and 10072 are similar to those of 10024 and 10022, respectively. The terms dolerite and

Fig. 1. Photomicrograph of the Ca  $K\alpha$ emission of one type of intergrowth of augite (light areas) and pigeonite (dark areas) in 10024. One edge of the photograph corresponds to 80 µm.

microgabbro (or dolerite pegmatite) would be appropriate for 10022 and 10024, respectively. However, peculiar textures such as the radial and fine intergrowth of augite and plagioclase and of augite and pigeonite are unlike those in the terrestrial dolerites and microgabbros.

In the pyroxenes augite-subcalcic ferroaugite predominates over pigeonite in amount. No orthopyroxene was found. Pigeonite is closely associated with augite and often occurs as rounded or irregularly elongated inclusions in augite. One type of the intergrowth of both the clinopyroxenes is shown in Fig. 1. Similar intergrowth of needlelike augite and plagioclase is often observed. These intergrowths are indicative of rapid growth of clinopyroxenes and plagioclase. Some of the very fine intergrowth of augite and pigeonite may be a result of the rapid exsolution of metastable subcalcic augite.

More than 50 complete analyses of clinopyroxenes have been made with the electron-probe microanalyzer (2). The greater parts of the augite-subcalcic ferroaugite crystals are titaniferous augite with  $TiO_2$  2 ~ 3 percent by weight; however, marginal parts of many crystals abutting on mesostasis are very rich in Fe and poor in Ca, Mg, and Ti. The plot of clinopyroxene analyses in the Ca-Mg-Fe diagram (Fig. 2) shows that the compositional variations are very large, with a trend toward ferrosilite. The most iron-rich one, which is yellowish in thin section, is close to ferrosilite, its composition being outside the compositional areas of subcalcic ferroaugite and ferropigeonite so far given (3). The large part of the compositional variation of clinopyroxene is observable in a single crystal, as shown in Fig. 2. Continuous scanning from the center to the margin of strongly zoned crystals with the  $K_{\alpha}$  emission of Ca, Mg, Fe, Ti, and Al has shown that the zoning is essentially continuous, although steep changes in Ca and Fe are observed within the distance of 10  $\mu m$  in the marginal zones of some crystals. The compositional range of pigeonite is not large compared with those of augite-subcalcic ferroaugite. Some of the tie lines between coexisting augite and pigeonite are drawn in Fig. 2. The partition coefficient  $K_{\rm D}$  of Mg-Fe (4) between the augite and pigeonite is  $0.90 \sim 1.01$ , with an average of 0.96, indicating the relatively high temperature of equilibration. The compositional

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Fig. 2 (left). Ca-Mg-Fe plot of the analyzed clinopyroxenes in 10022 in 10024. Solid lines indicate the ranges of compositional zoning within single crystals, dashed lines are tie lines between coexisting augite and pigeonite, and dotted lines indicate a possible miscibility gap between augite and pigeonite in 10024. Fig. 3 (right). Al-Ti relations of the analyzed clinopyroxenes in 10022 and 10024. Solid line indicates the ratio  $Ti/Al = \frac{1}{2}$ .

gap between augite and pigeonite is considerably smaller than those found in the terrestrial plutonic rocks. The clinopyroxenes which occur as needlelike crystals intergrown with plagioclase are poor in Ca and fall in the area intermediate between augite and pigeonite (Fig. 2). These subcalcic augites may have formed by rapid crystallization. They are most probably metastable because their compositions fall within the miscibility gap. The relatively iron-poor titanaugites in 10022 have higher Al and Ti and lower Si than those in 10024. The Al-Ti relations of the analyzed clinopyroxenes are shown in Fig. 3. Augites crystallized from the more silica-undersaturated magmas have higher Al and Ti and lower Si content (5), and the relative concentration of silica in the original magma of 10022 may therefore have been lower than that of 10024 when augite crystallized.

Olivine is found in 10022 and 10072. The compositional range of olivine in 10022, on the basis of the 11 microprobe analyses, is  $Fo_{71}Fa_{29} \sim Fo_{41}Fa_{59}$ . This compositional zoning is observable in a single crystal. Olivine has slightly higher Mg/Fe ratios than the contacting pigeonite and augite.

Four ilmenite crystals have been analyzed. They are close to stoichiometric FeTiO<sub>3</sub> but contain small amounts of Mg, Cr, Mn, and Zr and show little zoning.

Nine plagioclase crystals have been analyzed. Their compositions are between  $An_{73}Ab_{27}$  and  $An_{81}Ab_{19}$  in 10022 and  $An_{78}Ab_{22}$  and  $An_{80}Ab_{20}$  in 10024; that is, they are all bytownite. Many other plagioclase crystals were examined by scanning and found to be essentially homogeneous. In some crystals, however, weak zoning to sodic bytownite was observed at the margins. Those

which occur in the mesostasis are also sodic bytownite.

Semiquantitative analysis shows that a relatively large native iron crystal in a troilite of 10024 contains 0.6 percent Ni by weight.

Mesostasis is dark in transmitted light. The grain size of the phases in the mesostasis varies from 1 to 20  $\mu$ m. These phases, identified by the microprobe, are described above. The potassium-rich phase, which is most probably glass, has the following composition (percent by weight): SiO<sub>2</sub> 75  $\sim$ 80; Al<sub>2</sub>O<sub>3</sub>, 10; CaO, 1; Na<sub>2</sub>O, < 0.5; K<sub>2</sub>O, 9. From the textural relations the mesostasis is considered to have crystallized in the latest stage of crystallization of the rocks; that is, it represents the residual liquid. The microprobe analysis with a large beam size  $(20 \mu m)$  was made to obtain the bulk composition of the mesostasis. Because of the pres-



Fig. 4. Melting relations of a lunar crystalline rock (type A); (left) 0.5 mm; (right), 0.12 mm (horizontal dimensions). 30 JANUARY 1970

ence of the potassium-rich glass, most of the mesostasis have high potassium contents, although the relative amount of the glass is different in different mesostasis. One of the 10 analyses is as follows (percent by weight): SiO<sub>2</sub>, 71; TiO<sub>2</sub>, 1.1; Al<sub>2</sub>O<sub>3</sub>, 11.5; FeO, 6.1; MnO, 0.1; MgO, 0.2; CaO, 2.4; Na<sub>2</sub>O, 0.7; K<sub>2</sub>O, 6.6; total, 99.7. It is of interest that the mesostasis is granitic or rhyolitic in composition, though the sodium content is considerably lower and the iron content is higher than in most terrestrial granites. Absence of Kfeldspar in the mesostasis indicates that the temperature of the solidification of the mesostasis was at least above the plagioclase-K-feldspar-silica quaternary minimum.

The rapid-growth texture and the presence of metastable clinopyroxenes suggest that most of the rock crystallized rapidly. During the crystallization of the magmas, clinopyroxenes and olivine change considerably in composition, whereas plagioclase changes very little and stays as bytownite. These features are similar to those observed in the chilled zones of the prehistoric Makaopuhi lava lake studied by Evans and Moore (6), although the compositional variation of augite is narrower and that of plagioclase is wider in Makaopuhi than in 10022 and 10024. Evans and Moore suggest that the narrow compositional range of plagioclase in the chilled zones as compared with those in the slowly cooled zones is due to the relatively rapid crystallization of the undercooled magma. In view of the cooling history in the Makaopuhi lava lake, it is suggested that the lunar rocks 10022 and 10024 were also formed by crystallization of undercooled magmas. In this case crystallization would have been rapid. During the crystallization, fractional crystallization of ferromagnesian minerals took place, and the residual liquids were enriched in silica and potassium and other minor elements such as phosphorus, sulfur, and zirconium. Thus, rhyolitic liquids were formed in the last stage of the crystallization. The presence of native iron indicates that the oxygen pressure was low during the crystallization.

The melting experiments were made at 1 atm and at high pressures. A fine-grained crystalline rock of type A which was separated from the fines 10085,13 and numbered 10085,13-1 and a type B rock, 10017,66, were used. The bulk chemical compositions, deter-

mined by wet chemical method, are as follows, in percent by weight for 10017, 66 and 10085,13-1, respectively:  $SiO_2$ , 40.03 and 40.16; TiO<sub>2</sub>, 11.61 and 11.93;  $Al_2O_3$ , 8.04 and 7.50;  $Fe_2O_3$ , 0.0 and 0.0; FeO, 20.46 and 20.37; MnO, 0.24 and 0.26; MgO, 8.17 and 8.09; CaO, 10.26 and 10.17; Na<sub>2</sub>O, 0.49 and 0.53; K<sub>2</sub>O, 0.30 and 0.29; H<sub>2</sub>O, 0.0 and not detected;  $P_2O_5$ , 0.17 and 0.15;  $Cr_2O_3$ , 0.34 and 0.42; NiO, 0.00 and not detected; totals, 100.11 and 99.87 (7).

The melting experiments at atmospheric pressure were made by the quenching method under controlled oxygen partial pressure of 10<sup>-8</sup> to 10<sup>-13</sup> atm. Pt-40-percent-Rh and Ag-40percent-Pd crucibles were used as sample containers. In some of the runs Fe-saturated Pt-40Rh crucibles were used to prevent iron loss from the sample. The high-pressure experiments were made with the tetrahedral-anvil type apparatus described by Akimoto et al. (8). The lunar sample, which was ground finely in an agate mortar, was put in molybdenum capsule. Temperature was measured with Pt/Pt-13percent-Rh thermocouple. The phases after the runs were identified with both the microscope and electron-probe microanalyzer.

Melting relations of rock 10085,13-1 are given in Fig. 4. At 1 atm chromite and chromian (Mg,Fe)Ti<sub>2</sub>O<sub>5</sub> are on the liquidus in the runs made with the Pt-40Rh crucible; however, only chromite is on the liquidus in the run made with the Fe-saturated Pt-40Rh crucible. In the former runs, the crucible was found to dissolve considerable amounts of iron from the samples. This may explain the crystallization of chromian (Mg,Fe)Ti<sub>2</sub>O<sub>5</sub> near the liquidus temperatures. The runs made with the Fesaturated Pt-40Rh crucible show that the liquidus temperature of the present lunar rock is slightly above 1200°C. In the run made with the Ag-40Pd crucible at 1160°C, a small amount of chromian  $(Mg,Fe)Ti_2O_5$  was observed with clinopyroxene, as in the runs made with the Pt-40Rh crucible. Since the Ag-40Pd crucible is believed to dissolve much less iron than the Pt-40Rh crucible, the chromian  $(Mg,Fe)Ti_2O_5$ might be a phase crystallizing from the liquid of lunar rock composition. On the basis of the runs made with the untreated Pt-40Rh crucible, the sequence of crystallizing phases is chromian (Mg,Fe)Ti<sub>2</sub>O<sub>5</sub> and chromite, Carich clinopyroxene, olivine, ilmenite,

plagioclase with lowering temperature. At 1125° and 1130°C both chromian  $(Mg,Fe)Ti_2O_5$  and ilmenite crystallized, whereas at 1100°C ilmenite but no chromian (Mg,Fe)Ti<sub>2</sub>O<sub>5</sub> crystallized. Since chromite and chromian (Mg,Fe)  $Ti_2O_5$  were not found in rock 10085, 13-1, the rock would have crystallized at temperatures below 1125°C if it crystallized near the surface of the moon.

At high pressures the liquidus phases for the 10085,13-1 composition are different from those at 1 atm: At 20 and 30 kb, Ca-rich clinopyroxene and rutile crystallize slightly below the liquidus, and at 40 kb Ca-rich clinopyroxene is on the liquidus. It is noted that no chromite and chromian (Mg,Fe)Ti<sub>2</sub>O<sub>5</sub> crystallize at high pressures. On the basis of the high-pressure runs it is suggested that the original magma of the rock 10085,13-1 could be formed by partial melting of materials containing clinopyroxene and rutile in the depths of the moon. Of course other hypotheses involving formation of the rock by the fractional crystallization of magmas with lower Fe/Mg ratio are also possible.

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